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Infrared Luminescence of Ytterbium Ion in Complexes with Calix[4]resorcinarenes

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New ytterbium complexes with seven calix[4]resorcinarenes containing methoxycarbonyl, methyldiethylamino groups, and bromine as the substituents in the resorcinol ring and methyl or phenyl substituents in the macro ring were synthesized. The absorption, excitation, phosphorescence, and luminescence spectra of these complexes were studied. The positions of triplet levels of the ligands were measured and the values of relative quantum yields for the complexes were calculated. The paths of ligand–lanthanide energy transfer are discussed.

KEY WORDS: Ytterbium complexes; calix[4]resorcinarenes; absorption; luminescence.

INTRODUCTION

The ability of calix[*n*]arene structures to encapsulate lanthanide ions effectively and the appearance of Ln^{3+}-intensive luminescence in these complexes have attracted the attention of many scientists because of their possible applications for various analytical and biochemical purposes [1,2]. Now the calix[*n*]arenes are considered as potential ligands, mainly, to obtain the energy-transfer luminescence of Tb^{3+}ions. High-emitting systems for terbium ion were developed with sulfonate [1,3], tetraacetamide [4], and phenyl and biphenyl calix[*n*] arene [5] derivatives and the processes of ligand–lanthanide ion energy transfer were studied. Recently, we reported some spectral-luminescence properties of ytterbium complexes with tetradimethylamino derivatives of calix[4]resorcinarenes [6]. Previously it was shown that the luminescence of Yb^{3+} ion in complexes with resorcinol dyes arises from ligand-to-lanthanide ion excitation energy transfer [7].

This work deals with the study of some absorption and luminescence characteristics of ytterbium complexes with seven calix[4]resorcinarenes (L_1–L_7) containing methyldiethylamino and methoxycarbonyl substitutents in the resorcinol ring and methyl and phenyl ones in the macro ring. The structures of the ligands are presented in Fig. 1.

EXPERIMENTAL

Ytterbium oxide, paraformaldehyde, resorcinol, acetic aldehyde, and benzoaldehyde were purchased from Aldrich (Gillingham, Dorset) and used as received. All other chemicals were analytical-grade reagents. The 1×10^{-4} mol dm^{-3} solutions of complexes were prepared by dissolving the accurate weights of the solid compounds in the solvents required. Lower concentrations were obtained by dissolving these solutions with the solvents. The syntheses of ligands $L_{1,2}$ [6] and L_{3-6} [8,9] were described previously. The initial compound for synthesis of ligand L_7 was tetrabromocalix[4]resorcinarene [10] that was acylated by the method reported elsewhere [8]. The purity of prepared com-

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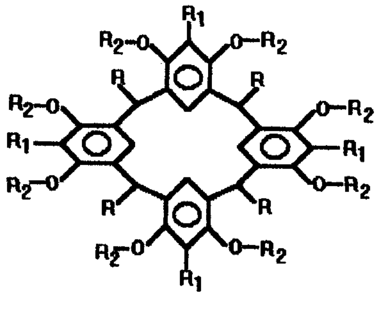

	R	R_1	R_2
L_1:	C_6H_5	$CH_2\text{–}N(C_2H_5)_2$	H
L_2:	CH_3	$CH_2\text{–}N(C_2H_5)_2$	H
L_3:	CH_3	H	H
L_4:	CH_3	H	$COCH_3$
L_5:	C_6H_5	H	H
L_6:	C_6H_5	H	$COCH_3$
L_7:	CH_3	Br	$COCH_3$

Fig. 1. Structures of the ligands studied.

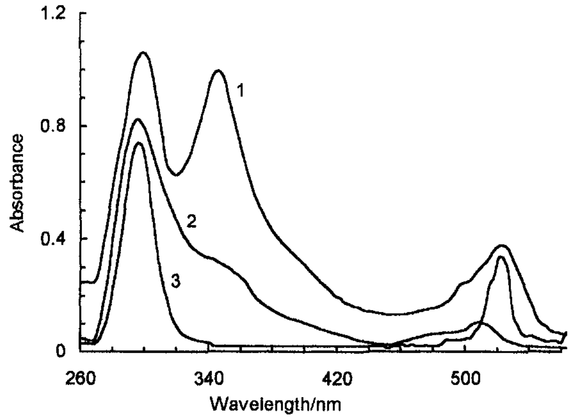

Fig. 2. Absorption spectra of L_1 (1) and its ytterbium complex (2) and excitation-corrected spectrum of complex (3) in ethanol solutions. $C_{Yb} = 1 \times 10^{-4}$ mol dm^3, λ_{em} = 978 nm, room temperature.

pounds was controlled by ^{1}H NMR, mass spectroscopy, and TLC.

Absorption spectra of ligand and complex solutions were recorded on Specord M-40 UV/VIS and Lambda 9 UV/VIS/NIR spectrophotometers. Luminescence measurements were carried out on an SDL-2 spectrofluorimeter equipped with a photon counting system and a chamber for phosphorescence measurements (Leningrad Optic-Mechanical Association, St. Petersburg, Russia) [11]. The spectra were corrected with a standard lamp. A xenon lamp was used as the excitation source. The positions of ligand triplet levels were obtained from phosphorescence spectra of ligands in complexes with lutetium at 77 K that were excited at 300 nm (L_{1-7}), 520 nm (L_1), and 512 nm (L_2). The quantum yields for ytterbium ion (λ_{exc} =300 nm) in complexes were calculated by the relative method [12] using Zn–tetraphenylporphyrin as a standard, the quantum yield of which is 0.0315 [13].

RESULTS AND DISCUSSION

Absorption spectra of ligands L_1–L_7 in ethanol solutions are characterized by the presence of strong bands (extinction coefficients, $\varepsilon \approx$ 9000–13,000) in the UV region corresponding to the transitions in aromatic groups. Ligands L_1 and L_2 also contain weaker bands ($\varepsilon \approx$ 3000–5000) in a range of 480–590 nm. This absorbance in the visible region may be ascribed to the formation of intramolecular hydrogen bonds between nitrogen atoms of methyldiethylamino groups and hydrogen atoms of OH groups of the resorcinol ring as a result of the essential redistribution of electron density takes play, causing the delocation of π-electrons through the H-bridge [14]. These bands for the ytterbium complexes are significantly changed in shape and their maximums are shifted by 2–65 nm ($\Delta\lambda$) relative to the free ligands. For instance, Fig. 2 demonstrates the absorption spectra of free L_1 and its ytterbium complexes. Data for all the complexes are presented in Table I. The observed differences in these spectra indicate that complexation takes place in the systems studied.

It was found that all complexes may be excited at 290–300 nm (Fig. 2). The complexes of ligands L_1 and L_2 also possess excitation at 520 and 512 nm, respectively. As can be seen from Fig. 2, there is a similarity between the absorption spectrum of the ligand and the excitation spectrum of the complex, indicating that ligand–lanthanide ion energy transfer takes place. For the Yb^{3+}–L_1 and Yb^{3+}–L_2 complexes the energy transfer can occur through both aromatic moieties and methyldiethylamino ones. The similar pattern was observed for terbium and europium complexes with calix[4]arenes modified by phenacyl or diphenacylcarbonyl groups, where the energy excitation was transferred not only from the phenol unit but also from the units of modifying groups [5].

Table I. Some Spectral-Luminescence Characteristics of L_1–L_7 and Their Complexes

	Absorption maxima (nm)			Position of triplet levels,	
Ligand/complex	Ligand	Complex	$\Delta\lambda$ (nm)	E (cm^{-1})	$\varphi \times 10^{-4}$
L_1	296	298	2	18,400	
	349	352	3		9.5
	500	487	−13		
	525	555	30	17,700	
L_2	294	298	4	19,000	
	360	350	−10		8.6
	480	—	—		
	512	575	65	17,900	
L_3	280	290	10	18,800	6.8
L_4	270		10		
		280		19,500	6.1
	275		5		
L_5	287	290	3	18,200	3.7
L_6	275		10		
		285		18,500	3.3
	280		5		
L_7	280		15		
		295		19,000	2.6
	290		5		

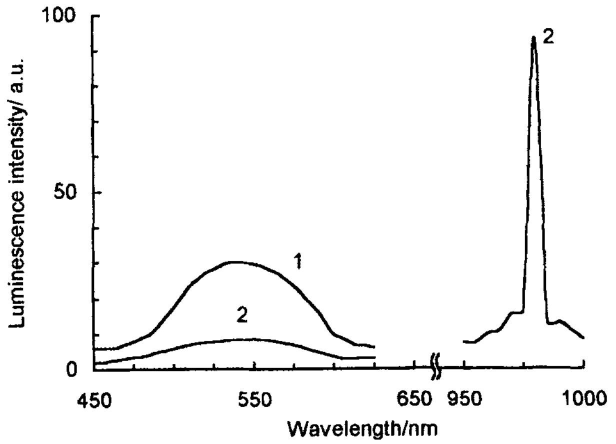

Fig. 3. Corrected luminescence spectra of ligand L_4 (1) and its ytterbium complex (2) in ethanol solutions. $C_{Yb} = 1 \times 10^{-4}$ mol dm^3, λ_{exc} = 300 nm, room temperature.

From the phosphorescence spectra of lutetium complexes we measured the positions of ligand triplet levels that situate in the range of 18,200–19,500 cm^{-1} for the resorcinol unit (L_{1-7}) and 17,700–17,900 cm^{-1} for the methyldiethylamino unit ($L_{1,2}$) (Table I). These results show that ligands L_1–L_7 are able to transfer effectively excitation energy to the Yb^{3+} ion, the emitting level of which is at 10,200 cm^{-1} (E) [7].

All the ligands display luminescence upon excitation at both 300 nm (L_{1-7}) and 520 nm (L_1) or 512 nm (L_2). Their luminescence bands are situated in the range of 400–600 nm. This ligand luminescence is significantly reduced in complexes confirming effective energy transfer from the organic moiety of the molecule to the lanthanide ion.

The metal-centered 4f luminescence of Yb^{3+} in complexes appears in the near-IR region at 978 nm and corresponds to the $^2F_{5/2} \rightarrow {}^2F_{7/2}$ transition. For instance, Fig. 3 shows the luminescence spectra of L_4 and Yb^{3+}–L_4 in ethanol solutions. When the ytterbium complexes of L_{1-7} were synthesized with various amounts of the reagents, it was found that maximal luminescence intensity is achieved with a ratio of Yb^{3+}:L_{1-7} equal to 1:1. The values of the relative quantum yields (ϕ) for ytterbium ion in the complexes considered are given in Table I. As can be seen from Table I, the Yb^{3+}–L_1 and Yb^{3+}–L_2 complexes show the highest quantum efficiencies compared with the others. The complexes of L_3 and L_4 also demonstrate high ϕ values, and weaker quantum efficiency is observed for complexes of L_5–L_7. However, all these values significantly exceed those reported previously for some ytterbium porphyrinates [13,15].

It should be noted that methyl and phenyl substituents in the macro ring affect differently the quantum efficiency in methyldiethylamino (L_1, L_2) and nonsubstituted (L_3, L_5) or methoxycarbonyl (L_4, L_6) calix[4]resorcinarene derivatives. Thus, complexes of L_1 containing phenyl substituents possess a higher quantum yield than that of L_2 with methyl substituents. The inverse pattern is observed for L_3 and L_5 as well as L_4 and L_6 complexes: ϕ values in Yb^{3+}–L_3 and Yb^{3+}–L_4 are larger than in Yb^{3+}–L_5 and Yb^{3+}–L_6, respectively. The bromine substituent in the resorcinol ring in L_7 reduces the quantum yield by 2.3 times compared with the Yb^{3+}–L_4 complex noncontaining one. Evidently, in this instance an effect of the inner "heavy atom" takes place, consisting in the change of the probability of energy interconversion into the complex triplet state [16].

CONCLUSIONS

The ytterbium ion in complexes with studied calix[4]resorcinarenes exhibits metal-centered 4f luminescence upon ligand excitation. Ligands L_1 and L_2, containing methyldiethylamino units in the resorcinol ring and phenyl and methyl groups in the macro ring, are the most favorable for ligand–lanthanide ion energy transfer for ytterbium ion. In the future, we intend to improve the luminescence characteristics of ytterbium complexes with calix[4]resorcinarenes by introducing other substituents absorbing in the visible spectrum region for their application as luminescence labels in immunofluorescence assays.

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